

Flame retardancy of glucofuranoside based bioepoxy and carbon fibre reinforced composites made thereof

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Abstract

Flame retarded bioepoxy resins and carbon fibre reinforced composites were prepared from a novel glucofuranoside based trifunctional epoxy monomer (GFTE) cured with aromatic amine hardener. 4% phosphorus (P)-containing samples were prepared using liquid resorcinol bis(diphenyl phosphate) (RDP), solid ammonium polyphosphate (APP), and their combination. The common application of the inorganic APP and the organophosphorus RDP had two main advantages: APP compensated the plasticizing effect of low P-containing RDP, resulting in increased glass transition and storage modulus values compared to RDP-containing sample, while RDP added gas phase flame retardant action to the APP acting only in the solid phase, resulting in self-extinguishing, V-0 UL-94 rated bioepoxy matrix and composite specimens.

Keywords: glucose-based bioepoxy; carbon fibre reinforced composite; flame retardancy; synergism; glass transition temperature; mechanical properties

1 Introduction

The development of polymer composite systems from renewable resources is one of the most commonly investigated research areas in the field of materials science. While in the case of the thermoplastic polymers, the dominance of poly(lactic acid) is doubtless [1,2], the optimal candidate of bio-based thermosetting material is still missing. The epoxy monomers, prepared from vegetable oils [3,4,5] or from lignin [6,7,8,9], are extensively studied in the literature; however, both systems have significant drawbacks, hindering their high-tech industrial spreading. The vegetable oil-based epoxy resins usually have low glass transition temperatures, which limits their potential fields of application, while the main disadvantage of the lignin-based materials is their hardly reproducible structure [10]. Among the materials of carbohydrate origin, the isosorbide-based epoxy monomer is in the focus of the researchers [11,12,13,14], but until now, no real break-through was reached.

The polymer composite industry (including electric, automotive and aircraft applications using *e.g.* high performance epoxy resins) also revealed the importance of renewable structures [15,16]. All-bio composites can be prepared by reinforcing bioresins with natural fibres [17]; however, several issues hinder their dispersion in high-tech applications, where the use of stiff parts with strictly constant parameters is indispensable. Thus, due to the low thermal stability, the fluctuating properties depending on the year and place of the harvest, or extraction method [18], and the high moisture-absorption of the natural fibres [19], in most cases carbon fibre-reinforced composites are applied. Although the research interest on renewable matrix materials is exponentially increasing in the last years, only few papers have been published about carbon fibre-reinforced bioepoxy composites [20,21,22].

The main drawback of the bio-based composites (similarly to the mineral oil based ones), aiming at the replacement of metallic structures, is their flammability during their use. In order to meet the strict safety requirements of more demanding sectors as electronic, automotive and aircraft industries, their flame retardant (FR) properties have to be improved, while maintaining other important characteristics, such as mechanical and thermal properties. Flame retardancy of polymers in the presence of carbon fibres however raises several issues to be addressed: Due to the high thermal conductivity of carbon fibres the ignition of the composites is facilitated (this phenomenon is known as candlewick effect). As FRs usually have a plasticizing effect, finding a balance between FR performance, glass transition temperature (T_g) and mechanical properties means a real challenge. Last, but not least the incorporated carbon fibres interfere in the mode of action of solid phase FRs [23], which has to be addressed as well. Phosphorus, depending on the molecular structure of the flame retardant, can act both in gas phase, mainly at the beginning of degradation, and later in solid phase, providing advantageous FR effect for biopolymers by this combined mechanism. In the gas phase, the $H\cdot$ and $OH\cdot$ radicals, responsible for the chain reaction of burning, can react with the formed $HPO\cdot$ and $PO\cdot$ radicals, leading to reduced reaction rate in the flame [24,25]. In the solid phase, the charring of the surface is promoted by the phosphorus compounds, resulting in a thermal insulating layer, which can protect the material from further degradation [26].

It is recognized, that it is favourable, if the applied flame retardant or flame retardant mixture acts both in gas and solid phase [27], furthermore, it is also suspected that the flame retardancy synergism of combining less volatile and more volatile phosphate FRs can be attributed to a combined phase action [28]. In our previous study [29] synergistic flame retardant effect of the combination of ammonium polyphosphate, acting in the solid phase as charring agent [26,30] and resorcinol bis(diphenyl phosphate) mainly acting as radical

scavenger in the gas phase [31] was systematically investigated in commercially available sorbitol polyglycidyl ether (SPE) bioepoxy resin. The synergistic effects were explained by a combined solid and gas phase mechanism (confirmed by thermogravimetric analysis, Fourier transform infrared analysis of the gases formed during laser pyrolysis, attenuated total reflection infrared analysis of the charred residues, as well as by mechanical resistance test of the chars obtained after combustion, performed in plate-plate rheometer).

In this work fire retardancy of a novel glucofuranoside-based trifunctional epoxy monomer (GFTE) and composite was attempted using APP, RDP and their combination. Fire retardancy of matrix and carbon fibre reinforced specimens was evaluated by limiting oxygen index (LOI), UL-94 tests and mass loss calorimetry. The thermal stability of the matrices was investigated by thermogravimetric analysis, while the effect of FRs on the glass transition temperature and crosslinking process was studied by differential scanning calorimetry in matrices and by dynamic mechanical analysis in composites.

2 Materials and methods

2.1 Materials

As epoxy (EP) monomer a novel, glucofuranoside-based trifunctional EP monomer (3,5,6-tri-*O*-(2,3-epoxypropyl)-1,2-*O*-isopropylidene- α -D-glucofuranoside, GFTE), synthesized and characterized previously by the research group of the authors [32,33]) was used (molecular weight: 388 g/mol, epoxy equivalent weight 160 g/eq, density 1.20 g/cm³, viscosity 3.77 Pas at 25 °C). Diethylmethyl-benzenediamine with 45 g/eq hydrogen equivalent (DETDA80 – DETDA), acquired from Lonza, was used as hardener. As flame retardant (FR) additives resorcinol bis(diphenyl phosphate) (RDP) (supplier: ICL Industrial Products, trade name: Fyrolflex RDP, P-content: 10.7%) and ammonium polyphosphate (APP) (supplier: Nordmann Rassmann, trade name: NORD-MIN JLS APP, P-content: 31-32%, average particle size: 15

μm) were applied. As reinforcement PX35FBUD030 type unidirectional carbon fibre (CF) fabric consisting of Panex 35 50k rovings, with 300 g/m^2 areal weight (from Zoltek Zrt.) was used.

2.2 Methods

Matrix sample preparation

During the specimen preparation in all cases stoichiometric ratio of EP component and hardener was used, the bio-based/ synthetic content (mass%) of GFTE matrix was 78/22. Epoxy resin samples of 3 (only for preliminary experiments due to low fire retardant performance) and 4 mass% phosphorus content were prepared. The composition of the GFTE reference and 4 mass% phosphorus-containing samples is summarized in Table 1. First, the flame retardant (FR) component (APP, RDP or both) was mechanically mixed with the GFTE epoxy component. The mixing time was adjusted to the homogenization of the mixtures: 5 minutes in the case of RDP 4%P sample, while in the case of the APP-containing samples the mixing was continued until the disappearance of the APP particles. Then the curing agent amine component was added and mixed for additional 5 minutes at room temperature in a crystallizing dish in order to obtain a homogenous mixture. The samples were cured in appropriately sized silicon moulds. Based on previous results on these matrices [33] the curing cycle consisted of three steps: 1h at $100 \text{ }^\circ\text{C}$, 1h at $150 \text{ }^\circ\text{C}$ and 2h at $175 \text{ }^\circ\text{C}$ heat treatment was applied. No visible aggregates of APP particles were observed in the cured samples.

Table 1 Composition of the GFTE reference and 4 mass% phosphorus-containing samples

Sample	GFTE	DETD	RDP	APP
	[%]	[%]	[%]	[%]
GFTE reference	78.05	21.95	0	0
RDP 4%P	49.16	13.82	37.02	0
APP 4%P	68.14	19.16	0	12.70
RDP 2%P+APP 2%P	58.65	16.49	18.51	6.35

Composite sample preparation

The composite laminates were made by hand lamination in a press mould. Each carbon weave layer was separately impregnated. The prepared laminates were put under compression with 180 bar hydraulic pressure (which equals to approx. 25 bar pressure on the laminate) in T30 type platen press (Metal Fluid Engineering s. r. l.) to achieve high and uniform fibre content in the composites. 2 mm thick laminates were made in [0]₅ layup. The heat treatment (same as in the case of the matrix samples) was carried out during pressing. The fibre content of the composites was in the range of 59-61 mass%.

Characterization of the fire behaviour

The fire behaviour of the reference and flame retarded systems was characterized by limiting oxygen index measurements (LOI, according to ASTM D2863). The LOI value expresses the lowest volume fraction of oxygen in a mixture of oxygen and nitrogen that supports flaming combustion of a material under specified test conditions. The sample size was 120 mm × 15 mm × 2 mm.

Standard UL-94 flammability tests (according to ASTM D3081 and ASTM D635, respectively) were also carried out in order to classify the samples based on their flammability in horizontal and vertical test setups. The UL-94 classifications range from least flame retardant HB, V-2, V-1 to V-0, self-extinguishing rate. The sample size was 120 mm × 15 mm × 2 mm.

Mass loss type cone calorimeter tests were carried out by an instrument made by FTT Inc. using the ISO 13927 standard method. Specimens (100 mm × 100 mm × 2 mm) were exposed to a constant heat flux of 25 kW/m² and ignited. Heat release values and mass reduction were continuously recorded during burning. From the recorded parameters peak of heat release rate (pHRR), total heat release (THR), fire growth rate (FIGRA), average effective heat of combustion (EHC), maximum of average rate of heat emission (MARHE) were calculated. In all cases lower values represent better FR performance.

Thermogravimetric analysis (TGA)

The thermal stability of the prepared FR matrix formulations was determined using a TA Q5000 device of TA Instruments in the range of 25-800 °C, with a heating rate of 20 °C/min, under nitrogen gas flow rate of 60 ml/min. Platinum-HT sample pan was used, the sample size was 5-10 mg in each case.

Differential scanning calorimetry (DSC)

The DSC tests were carried out with Q2000 device of TA Instruments in 50 ml/min nitrogen flow. Tzero type aluminium pans were used, the sample mass was 5-10 mg. For the investigation of the curing process of the samples the applied three-step temperature program consisted of heat/cool/heat cycles: after a linear ramp from 25-250 °C with 5 °C/min heat rate (first cycle), the sample was cooled down to 0 °C with 50 °C/min cooling rate, followed by a

second linear heating ramp from 0-250 °C with 5 °C/min heating rate (second cycle) to ensure the proper conversion. The glass transition temperature (T_g) values were determined from the second heating scan and were defined as the inflection point of the transition curve.

Dynamic mechanical analysis (DMA)

For the investigations of the dynamic mechanical properties and for the determination of the glass transition temperature (T_g) values of the carbon fibre reinforced composites DMA tests were carried out in three point bending setup with TA Q800 device of TA Instruments. The temperature range was 0-200 °C with 3 °C/min heating rate. The frequency was 1 Hz. The size of the specimens was 55 mm × 10 mm × 2 mm (length × width × thickness), and the support span was 50 mm. The amplitude was strain controlled with 0.1% relative strain. From the results glass transition temperature based on the tan delta peaks (T_g) and storage modulus (E') values at 25 °C and 75 °C were determined.

3 Results and discussions

3.1 Flame retardancy of the matrices

The reference GFTE cured with DETDA has an LOI of 22 V/V% and HB UL-94 rating, which can be considered as an average fire performance for an amine cured epoxy resin (the benchmark DGEBA cured with DETDA has somewhat higher, 24 V/V% LOI and HB UL-94 rating). Based on previous flame retardancy results with APP, RDP and their combinations in commercially available sorbitol polyglycidyl ether (SPE) bioepoxy matrix [29], first GFTE samples with 3 mass% P were prepared. Although their LOI increased significantly, especially in samples containing RDP, acting mainly in the gas phase, their UL-94 rate remained HB due to the flaming up to the holding clamp (Table 2). Similarly to the tendency in the case of LOI values, the samples containing RDP failed only during the 2nd vertical

ignition, while the APP 3%P sample flamed up to the clamp during the 1st ignition. Increasing the amount of P to 4 mass% resulted in significantly better UL-94 ratings: V-0 rate was reached both in RDP 2%P+APP 2%P and in APP 4%P samples. The LOI value of the APP 4%P sample reached the same level as the RDP-containing samples of 3% P-loading. Furthermore, from the two V-0 samples (APP 4%P and RDP 2%P+APP 2%P) the mixed FR formulation had 3 V/V% higher LOI (32 vs. 29 V/V%), which means that the combined solid and gas phase FR action is more favourable than the sole solid phase action of APP in this bioepoxy system as well.

Table 2 LOI and UL-94 results of the reference and flame retarded GFTE matrix samples

Flame retardant composition	LOI [V/V%]	UL-94 (burning rate)
GFTE reference	22	HB (25.6 mm/min)
RDP 3%P	30	HB (vertical 2 nd ignition)
APP 3%P	25	HB (vertical 1 st ignition)
RDP 1%P+APP 2%P	29	HB (vertical 2 nd ignition)
RDP 2%P+APP 1%P	29	HB (vertical 2 nd ignition)
RDP 4%P	31	V-1
APP 4%P	29	V-0
RDP 2%P+APP 2%P	32	V-0

Based on these results, in the followings only the reference and the 4 mass% P-containing samples were subjected to further analysis.

The heat release rate curves of the reference and flame retarded GFTE matrix samples can be seen in Fig. 1, while numerical data obtained from mass loss calorimetry results are

summarized in Table 3, best performances among the samples are highlighted with bold letters.

Table 3 Mass loss type cone calorimetry results of reference and flame retarded GFTE samples

Sample	TTI (s)	pHRR (kW/m ²)	Time of pHRR (s)	FIGRA (kW/m ² s)	Burning time (s)	THR (MJ/m ²)	EHC (MJ/kg)	MARHE (kW/m ²)	Residue (mass%)
GFTE matrix	54	361	93	3.9	155	44.4	21.0	173.5	6
RDP 4%P	44	211	81	2.6	196	26.0	14.5	110.5	19
APP 4%P	44	297	82	3.6	472	31.2	17.8	138.9	23
RDP 2%P+APP									
2%P	40	246	69	3.6	191	32.3	19	128.1	25

(TTI: time to ignition, pHRR: peak of heat release rate, FIGRA: fire growth rate, THR: total heat release, EHC: average effective heat of combustion, MARHE: maximum of average rate of heat emission)

average standard deviation of the measured mass loss calorimeter values: TTI: ±3, pHRR: ±30, time of pHRR: ±5, residue: ±2

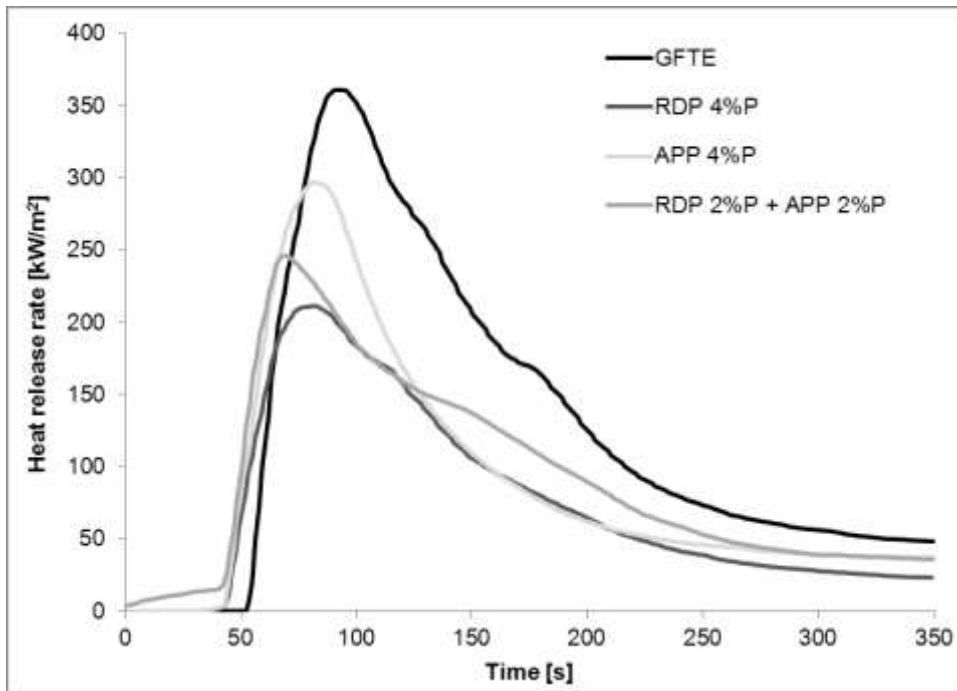


Fig. 1. Heat release rate of reference and flame retarded GFTE matrix samples

In all flame retarded samples, the TTI decreased compared to the reference GFTE matrix, which is in agreement with the lower thermal stability at the beginning of the thermal degradation showed by TGA (see Chapter 3.2). As for the heat release rate, the lowest pHRR was reached in the case of RDP 4%P, showing a reduction of about 40%. Surprisingly, the APP 4%P showed only a modest effect, while the pHRR value of the sample containing mixed FR formulation was between the values of the compositions containing only one FR. Regarding the FIGRA values, no significant difference was observed between the APP 4%P and the mixed FR sample, their result was only slightly better than that of the reference GFTE matrix, while the FIGRA of the RDP 4%P is only the one third of the reference value. Similarly, the difference between the THR values of the formulation containing only APP as flame retardant, and that containing both APP and RDP (showing a reduction of about 30% compared to the reference) is negligible. The lowest EHC value was reached in the case of RDP 4%P, followed by APP 4%P. In this respect, among the flame retarded samples, the mixed FR formulation was the less effective. Considering the amount of the charred residues,

the sample containing sole RDP, acting mainly in the gas phase had the least residue, as expected. Although the APP has only solid phase effect, in the case of the mixed FR formulation higher amount of charred residue was observed, indicating that the combined FR mechanism can more effectively protect the material. Summarizing the results of the mass loss calorimetry (Table 3), RDP 4%P showed the best overall performance, followed by the mixed formulation. Similarly to the LOI results, APP 4% P showed the most modest flame retardant action, suggesting that the solid phase action alone is not sufficient in this bioepoxy resin to provide significant flame retardant effect.

3.2 TGA of the matrices

The thermal stability of the reference and flame retarded GFTE matrix samples were examined by thermogravimetric analysis. Table 4 shows the temperature at 5% and 50% mass loss ($T_{-5\%}$; $T_{-50\%}$), the maximum mass loss rate (dTG_{max}), the temperature belonging to this value (T_{dTGmax}) and the char yield at the end of the TGA test (at 800 °C). The TGA curves in the temperature range from 25-800 °C are displayed in Fig. 2.

Table 4 TGA results of flame retarded GFTE matrix samples

Flame retardant composition	$T_{-5\%}$ [°C]	$T_{-50\%}$ [°C]	dTG_{max} [%/°C]	T_{dTGmax} [°C]	Char yield [%]
GFTE	348	373	-2.5	362	11.9
RDP 4%P	269	373	-0.7	291	29.9
APP 4%P	311	369	-1.3	337	23.4
RDP 2%P+APP 2%P	300	409	-2.2	318	33.4

$T_{-5\%}$: temperature at 5% mass loss, $T_{-50\%}$: temperature at 50% mass loss; dTG_{max} : maximum mass loss rate; T_{dTGmax} : the temperature belonging to maximum mass loss rate

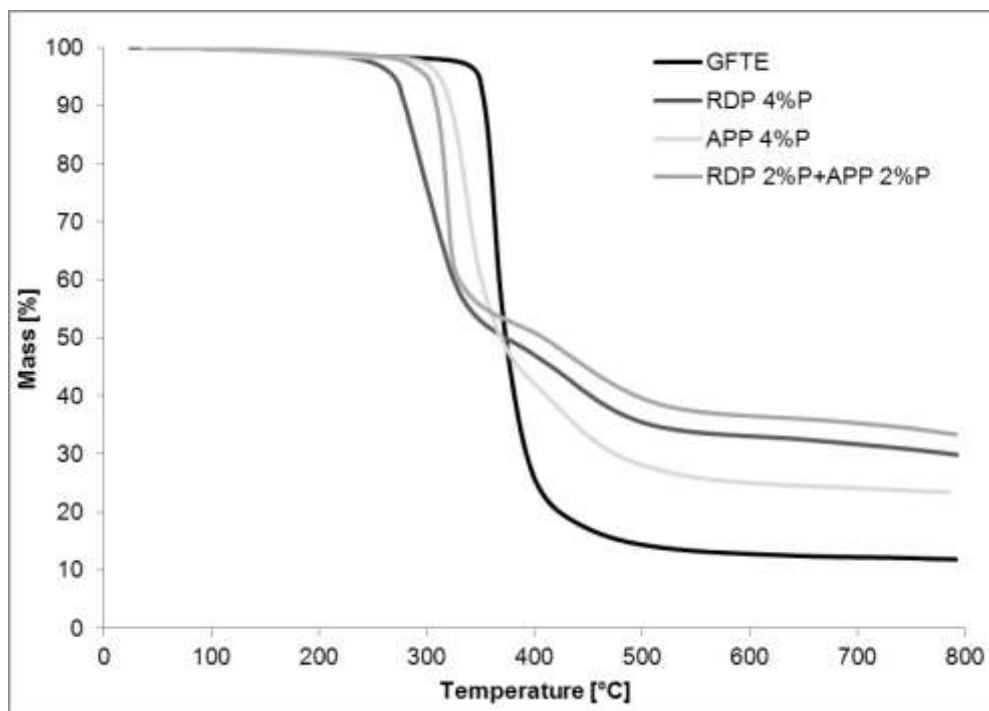


Fig. 2. TGA curves of the reference and flame retarded GFTE samples

According to the TGA results, the beginning of thermal degradation of the flame retarded samples is shifted to lower temperatures, especially in the case of samples containing RDP, acting mainly in gas phase during the early stage of the degradation, resulting in almost 80 °C lower $T_{-5\%}$ value. In the case of the APP, the decrease is less pronounced; the $T_{-5\%}$ is only 37 °C lower than that of the reference GFTE, while the mixed FR formulation lies between the samples containing only one FR. The degradation of the reference GFTE sample starts with a sudden mass loss, showing the highest mass loss rate among the samples. The APP 4%P and RDP 4%P samples show moderate, prolonged degradation, with significantly decreased dTG_{max} values. Surprisingly, the degradation of the combined FR containing RDP 2%P+APP 2%P sample starts with almost the same mass loss rate value as the reference GFTE, on the other hand, after this first sudden mass loss, the further degradation of the mixed FR formulation is much more balanced, insofar as the highest $T_{-50\%}$ temperature belongs to this sample (409°C). The char yield of the flame retarded samples is significantly increased,

compared to the reference GFTE. The compositions containing RDP show somewhat higher values than the sole APP-containing sample, which can be explained by the aromatic structure of the RDP: almost 90 mass% of the molecule is composed of phenol and resorcinol, which thus increase the aromatic character of the charred residue [29]. Above 350 °C, the mixed formulation has the best thermal stability along with the highest char yield.

3.3 Effect of the additive flame retardants on the glass transition temperature and curing

In order to study the effect of the applied FRs on the glass transition temperature (T_g) and curing process, GFTE bioepoxy samples were subjected to DSC analysis.

Usually, the addition of FRs considerably influences the T_g of the matrix polymer, and subsequently its applicability as well. The T_g of the flame retarded GFTE samples determined by DSC can be seen in Table 5.

Table 5 Effect of the additive flame retardants on the glass transition temperature (T_g), reaction enthalpy and temperature belonging to exothermic peak in the case of GFTE samples

Flame retardant composition	T_g [°C]	Reaction enthalpy [J/g]	Reaction enthalpy [J/g epoxy]	Exothermic peak [°C]
GFTE reference	176	333	333	168
RDP 4%P	87	150	238	179
APP 4%P	175	264	302	167
RDP 2%P+APP 2%P	119	200	267	173

The plasticizing effect is more pronounced in the case of liquid RDP, by adding 4% P from the T_g became half of the original value. The T_g of the APP-containing sample practically

remained the same, which can be explained by two facts: Due to the higher P-content, less amount of APP is needed to reach the same P-content as in the case of RDP (see Table 1). Furthermore, according to previous results [34], well-dispersed rigid APP particles can block the segmental movements in the cross-linked epoxy resins and can consequently compensate the T_g decrease initiated by the presence of filler particles. The T_g of the combined FR sample was between the values of the single FR formulations.

As for the effect on the crosslinking process, the temperatures belonging to the exothermic peak of curing show no significant difference; in the case of RDP-containing samples the curing process is slightly shifted to higher temperatures. Again, due to the high amount needed from RDP to reach 4 mass% P-content, RDP significantly reduces the reaction enthalpy of crosslinking, as expected. In order to have a clear comparison of the effect of APP and RDP on the curing process, reaction enthalpies related to g epoxy resin matrix (disregarding the mass of the added fillers) were compared as well. According to these results, the inclusion of RDP to reach 4% P-content resulted in approximately 30% reduction, while in the case of APP this reduction was only 10%.

3.4 Flame retardancy of the composites

The LOI and UL-94 results of the flame retarded composites can be seen in Table 6. The heat release rate curves are displayed in Fig. 3, while numerical data obtained from mass loss calorimetry results are summarized in Table 7, best performances among the samples are highlighted with bold letters.

Table 6 LOI and UL-94 results of the flame retarded GFTE composites

Flame retardant composition	LOI [V/V%]	UL-94 (burning rate [mm/min])
GFTE composite	22	HB (32.2 mm/min)
RDP 4%P	40	V-0
APP 4%P	30	HB (2 nd ignition)
RDP 2%P+APP 2%P	30	V-0

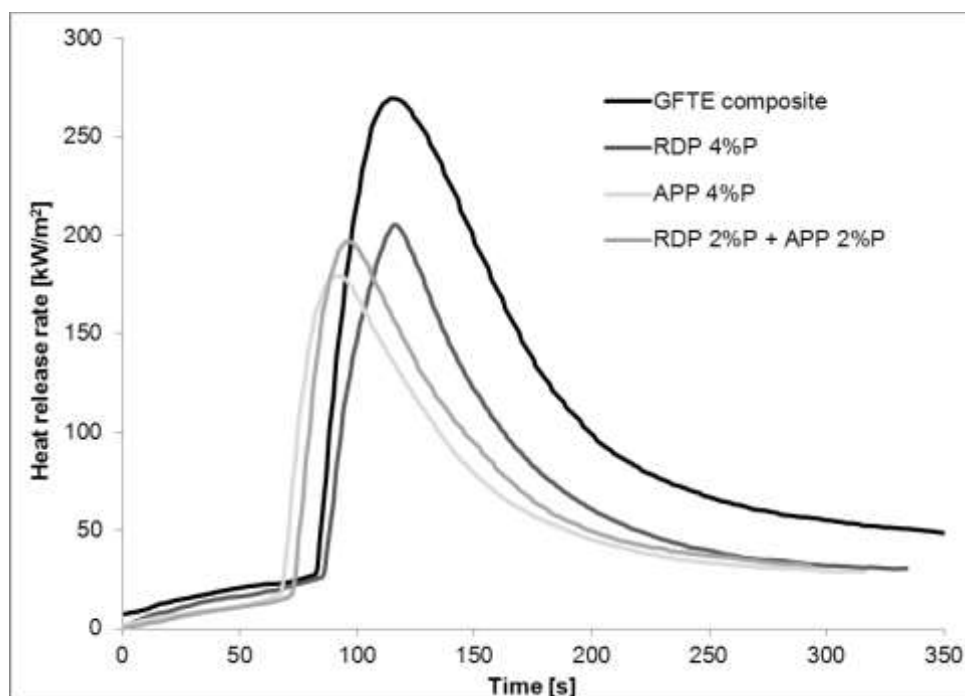


Fig. 3. Heat release rate of reference and flame retarded GFTE composites

According to the LOI and UL-94 results, despite the inclusion of inert carbon fibres, the GFTE composite had the same LOI as the matrix itself, and even its burning rate increased, due to the so called candlewick effect of the fibres with good heat conductivity. As carbon fibre reinforcement also hinders the intumescent action of solid phase flame retardants [23], in the case of the APP containing composite the UL-94 rating remained HB, despite the high P-

content. To reach V-0, the inclusion of RDP was necessary, indicating that the ignitability of the samples highly depends on the gas-phase effect of the applied flame retardant. The RDP 4%P sample reached an outstanding LOI of 40 V/V% compared the 22 V/V% value of the GFTE reference.

According to mass loss calorimetry results, all composite samples ignited later (TTI increased by 24-41 s) and the time of pHRR was reached later (by 10-35 s) than in the case of the matrix samples. By the inclusion of carbon fibres the pHRR was reduced to the greatest extent in the APP 4% P composite (by 40%), while in RDP 4% sample practically no further reduction of pHRR could be achieved. Between the flame retarded composites no significant difference was observed: they had by approx. 30% reduced pHRR and THR values compared to the GFTE reference composite, as well as the ECH and MARHE decreased by one third, when flame retardant was applied, indicating that the differences between the different FR formulations are obscured by the inclusion of the inert carbon fibre reinforcement. In the case of APP-containing samples the ignition occurred earlier than is case of RDP-containing ones and the reference, which may be interpreted with the hindered intumescent action through carbon fibre reinforcement. However, once the protective coating is formed, the HRR is efficiently reduced, leading to the lowest pHRR (but still in the range of the standard deviation of the measurement), THR, EHC, MARHE values and highest amount of residue. The mixed formulations shows only a slightly lower performance, but taking into consideration, that it has a V-0 UL-94 rating, compared to the HB rating of APP 4%P sample, the overall performance of the combined formulation is better.

Table 7 Mass loss type cone calorimetry results of reference and flame retarded GFTE samples

Sample	TTI (s)	pHRR (kW/m ²)	Time of pHRR (s)	FIGRA (kW/m ² s)	Burning time (s)	THR (MJ/m ²)	EHC (MJ/kg)	MARHE (kW/m ²)	Residue (mass%)
GFTE composite	83	270	115	2.3	108	32.6	25.5	116.0	42
RDP 4%P	85	205	116	1.8	104	20.6	17.3	77.8	49
APP 4%P	68	179	92	1.9	104	18.0	16.3	74.1	54
RDP 2%P+APP									
2%P	71	197	96	2.0	87	18.4	16.3	77.4	53

(TTI: time to ignition, pHRR: peak of heat release rate, FIGRA: fire growth rate, THR: total heat release, EHC: average effective heat of combustion, MARHE: maximum of average rate of heat emission)

average standard deviation of the measured mass loss calorimeter values: TTI: ± 3 , pHRR: ± 30 , time of pHRR: ± 5 , residue: ± 2

3.5 Dynamic mechanical properties of composites

Storage modulus curves of reference and flame retarded GFTE composites are displayed in

Fig. 4, while numerical results of dynamical mechanical analysis (glass transition

temperatures determined from the peak of tan delta, and storage modulus at 25 °C and 75 °C)

of the composites are shown in Table 8.

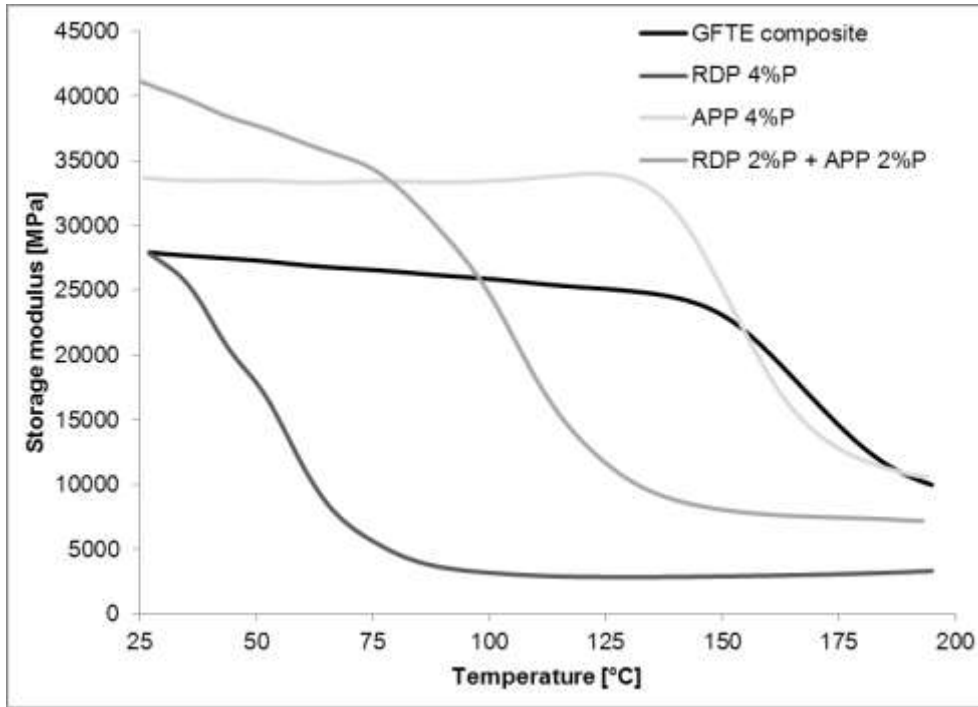


Fig. 4. Storage modulus curves of reference and flame retarded GFTE composites

Table 8 T_g values and storage modulus of reference and flame retarded GFTE composites

Flame retardant composition	T_g [°C]	Storage modulus at 25 °C [MPa]	Storage modulus at 75 °C [MPa]
GFTE composite	172	27938	26576
RDP 4%P	56	27853	5638
APP 4%P	156	33666	33411
RDP 2%P+APP 2%P	104	41134	34363

In the case of APP-containing samples approximately up to their T_g , their storage modulus is higher than that of the GFTE reference composite, which may be explained by the stiffening effect of dispersed rigid APP particles in the matrix. On the other hand, it has to be noted that the RDP-containing samples are already in the transition state at the beginning of the measurement. This can be interpreted again by the low P-content of RDP and thus its high

amount needed for appropriate flame retardancy, resulting in substantial plasticizing effect. The initial storage modulus of the mixed FR formulation, however, is the highest among the investigated composites. With increasing temperature, due the facilitated segmental movements, the plasticizing effect of the liquid RDP overcomes the stiffening effect of the APP particles, so the behaviour of the composite becomes similar to the sole RDP-containing one.

As for the glass transition temperatures, the decreasing tendencies are similar to those observed in the case of the matrices (Table 4); however the values are somewhat lower. The extent of T_g reduction due to the inclusion of carbon fibres increases in the following order: GFTE < RDP 2%P+APP 2% < APP 4%P < RDP 4%P. The incorporation of the flame retardants more polar than the epoxy resin matrix itself decreases the fiber matrix adhesion, leading to the reduction of T_g as well. Furthermore, due to the inclusion of the carbon fibres, the dispersion of the additives is probably not as uniform as in the case of the matrices, in the case of the solid APP even filtration may occur, resulting in less uniform crosslinking and somewhat lower T_g .

Conclusions

In this work the fire retardancy of the recently synthesized glucofuranoside based trifunctional bioepoxy monomer (GFTE) and carbon fibre reinforced composites made thereof was examined using two additive flame retardants (resorcinol bis(diphenyl phosphate) (RDP) acting mainly in gas phase and ammonium polyphosphate (APP) acting in solid phase) and their combination. According to the flame retardancy results of the GFTE matrices, the combined solid and gas phase FR action proved to be more favourable than the sole solid phase action of APP in this bioepoxy: from the formulations reaching V-0 UL-94 rate (RDP 2%P+APP 2%P and APP 4%P), the mixed formulation had 3 V/V% higher LOI. The HB

rated RDP 4%P sample had the lowest heat release rate, followed by the mixed formulation, while APP 4% P had the most modest flame retardant performance, suggesting that the solid phase action alone is not enough in this epoxy resin to achieve effective flame retardancy. Moreover, in carbon fibre reinforced composite the reinforcement also hinders the intumescent action of APP, so addition of RDP was necessary to reach V-0 UL-94 rate in composites as well. In terms of heat release rate, the mixed formulation showed slightly lower performance than the APP 4% sample, but as it has a V-0 UL-94 rating, compared to the HB rating of APP 4%P sample, the overall fire retardancy performance of the combined formulation is better. Due to the low P-content of RDP, and consequent high amount needed to reach 4 mass% P-content, RDP significantly reduced the reaction enthalpy of crosslinking, the glass transition temperature of the bioepoxy matrix and of the composite, as well as the storage modulus of the composite. Addition of APP compensated the plasticizing effect of RDP, as well-dispersed rigid APP particles can block the segmental movements in the cross-linked epoxy resins. Consequently, up to its glass transition temperature (104 °C) the mixed FR formulation had higher storage modulus than the GFTE reference composite.

Acknowledgements

This work was financially supported by the Hungarian Scientific Research Fund (OTKA K112644, OTKA K120592 and PD112166). A. Toldy acknowledges the financial support received through János Bolyai Scholarship of the Hungarian Academy of Science. The authors would like to thank Zoltán Biró, Tibor Czigány, József Karger-Kocsis, György Marosi and Péter Bakó from Budapest University of Technology and Economics for useful comments.

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